

AN ELECTROCATALYTIC CATHODE DEVICE OF PALLADIUM
AND IRIIDIUM ON A HIGH DENSITY OR POROUS CARBON
SUPPORT AND A METHOD FOR MAKING SUCH A CATHODE

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT (1) MARIA G. MEDEIROS and (2) ERIC G. DOW, citizens of the United States of America, employees of the United States Government and (3) RUSSELL R. BESSETTE and (4) JAMES M. CICHON citizens of the United States of America, residents (1) Bristol, County of Bristol, State of Rhode Island, (2) Barrington, County of Bristol, State of Rhode Island, (3) Mattapoisett, County of Bristol, Commonwealth of Massachusetts and (4) Stamford, County of Fairfield, State of Connecticut, have invented certain new and useful improvements entitles as set forth above of which the following is a specification:

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7 STATEMENT OF GOVERNMENT INTEREST

8 The invention described herein may be manufactured and used
9 by or for the Government of the United States of America for
10 Governmental purposes without the payment of any royalties
11 thereon or therefor.

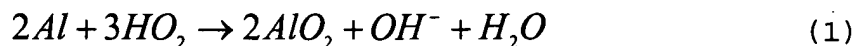
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13 BACKGROUND OF THE INVENTION

14 (1) Field of the Invention

15 The present invention relates to a method of producing an
16 improved carbon substrate cathode coated with palladium and
17 iridium which is highly efficient toward catholyte reduction and
18 is very stable.

19 (2) Description of the Prior Art

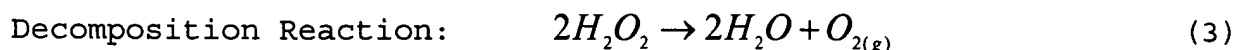
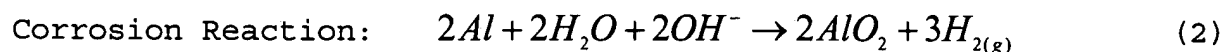
20 Aluminum anodes used in aqueous batteries with, for example,
21 silver (II) oxide or air cathodes have been extensively
22 investigated. The use of a hydrogen peroxide catholyte in
23 combination with an aluminum anode has been the subject of
24 several studies. When aluminum is combined with hydrogen
25 peroxide in a caustic electrolyte, the overall cell reaction is:



27 Operating cell voltages in the 1.2 - 1.7V range, depending on

current density, have been routinely obtained. The Al - H₂O₂ electrochemical couple compares favorably with the Al - AgO couple and other high energy density primary battery systems. An energy density of 360 Wh dm⁻³ is projected to be achievable for the Al - H₂O₂ solution phase catholyte system whereas an energy density of 290 Wh dm⁻³ is projected for a similarly configured Al - AgO system.

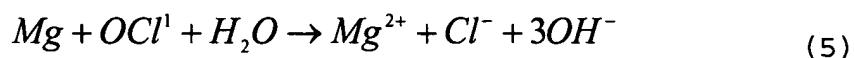
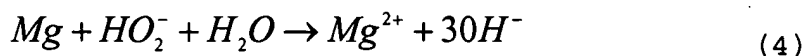
An ion diffusion membrane is not used in the semi-fuel cells studied to reduce complexity, weight, and cost while increasing reliability and cell voltage. The approach, however, results in the catholyte being in direct contact with both the anode and the electrocatalytic cathode substrate. A direct, non-electrochemical reaction will thus occur. Unless the rate of this direct reaction is low compared to the electrochemical anodic and cathodic reactions, the direct reaction will significantly reduce the overall efficiency of the cell. Additional reductions in efficiency can occur due to the corrosion reaction of aluminum with hydroxide ions and the decomposition reaction of H₂O₂.



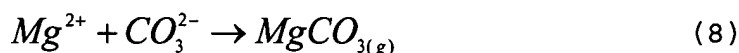
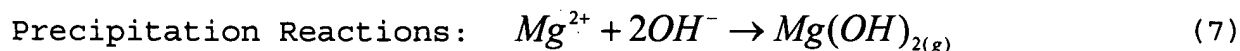
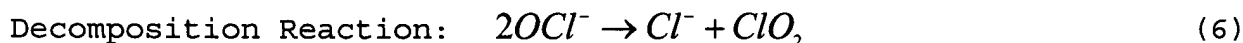
Improved catalysis for the reduction of H₂O₂ should result in reductions of the direct and the decomposition reactions, thus

1 improving significantly the electrochemical efficiency of the
2 cell.

3 A magnesium anode and either hydrogen peroxide or sodium
4 hypochlorite catholyte have also been investigated. The overall
5 cell reaction in each case is as follows:



9 Cell voltages in the 1.1 to 1.5V range have been obtained. Like
10 the aluminum-hydrogen peroxide system, these systems also are
11 operated without a membrane and thus have to be concerned with
12 the direct reaction of the catholyte (HO_2^- or OCl^-) with the
13 magnesium anode. The hypochlorite system also exhibits
14 decomposition and precipitation reactions.



20 Here again, improved catalysis will result in reduction of the
21 decomposition and precipitation reactions.

22 Several catalysts have been investigated for use in fuel
23 cells. Many of these catalysts (including palladium and iridium
24 independently) have been incorporated in carbon based pastes.

25 J.P. Collman and K. Kim, J. American Chemical Society, 108:24

26 (1986) 7847, have reported that iridium porphyrin complexes are

1 very active catalysts. Cox and Jaworski, J. Analytical
2 Chemistry, 61 (1989) 2176, have used a palladium-iridium
3 combination on a glassy carbon microelectrode for the
4 quantitative determination of H_2O_2 . A combination of palladium
5 and iridium has been shown to improve the electrochemical
6 efficiency for the reduction of H_2O_2 and to improve cell voltage
7 relative to the use of a metallic silver cathode.

8 Under high rate discharge (800 - 1000mA/cm²) efficient
9 electrochemical reduction of hydrogen peroxide (approximately 70%
10 coulombic efficiency) with a concomitant decrease in its
11 heterogeneous decomposition has been achieved through the use of
12 a Pd/Ir catalyzed cathode substrate. Efficiencies 30 to 40%
13 lower are obtained at current densities below 100 mA/cm². It
14 should be noted that applications of the Pd/Ir catalysis of a
15 nickel cathode substrate have been limited to high rate, single
16 use, short duration (less than 30 minutes) situations. When
17 attempts have been made to reuse the catalyzed nickel substrate,
18 performance changed with the second use and typically decreased
19 significantly with a third use.

20 The patent literature contains a number of patents related
21 to the manufacture of cathodes for use in chemical cells. These
22 include U.S. Patent Nos. 4,506,028 to Fukuda et al., 4,514,478 to
23 Binder et al., 5,296,429 to Marsh et al., 5,395,705 to Dorr et
24 al., and 5,578,175 to Lin et al.

1 The Fukuda et al. patent relates to an electrode substrate
2 for a fuel cell. The substrate is prepared by a process
3 comprising mixing 30 to 50 wt% carbon fiber, 20 to 50 wt% of a
4 binder, and 20 to 50 wt% of an organic granule, press-shaping the
5 resultant mixture, curing the shaped product, and calcinating the
6 cured product.

7 The Binder et al. patent relates to a porous carbon cathode
8 for use in an electrochemical cell. The cathode is made by
9 wetting the carbon black with a 1:1 to 1:3 mixture of isopropyl
10 alcohol:water, adding a binding agent thereto, smearing the
11 resulting stiff paste on a thin expanded metal screen and
12 pressing and rolling to a desired thickness, drying the cathode
13 sheet in a vacuum oven at about 100°C for one hour while a weight
14 is placed above and below the cathode sheet which is sandwiched
15 between two pieces of blotting paper, the total weight applied
16 being sufficient for the cathode to retain structural integrity,
17 removing the weight and blotting papers and inserting the cathode
18 sheet in an elevated drying oven at about 280°C for about one
19 hour, and cooling the cathode sheet between blotting paper,
20 repressing and rolling.

21 The Marsh et al. patent relates to an electrocatalytic
22 cathode which is comprised of nickel specially coated with one or
23 a combination of platinum, ruthenium, rhodium, osmium, palladium,
24 and iridium. The cathode is produced by pretreating a nickel
25 electrode with a hydrochloric acid bath and then by applying the
26 metal coating by plating methods.

1 The Lin et al. patent relates to a process for manufacturing
2 an iridium and palladium oxides coated titanium electrode. The
3 process comprises preparing a titanium substrate having a
4 surface, applying iridium and palladium to be formed on the
5 surface of the titanium substrate, and heat treating the iridium
6 and palladium oxides applied titanium substrate to obtain an
7 iridium and palladium oxides-coated titanium electrode.

8 The Door et al. patent relates to an electrochemical cell
9 having at least one electrode containing carbon fiber paper
10 coated with an uncoagulated mixture of binder and catalytically
11 active metal particles at catalyst/binder ratios of about 2/1 to
12 about 25/1. The metal catalyst particles include at least one of
13 the metals of Group VIII of the Periodic Table of Elements,
14 preferably rhodium, ruthenium, palladium, osmium, iridium, and
15 platinum (platinum black).

16 17 SUMMARY OF THE INVENTION

18 Accordingly, it is an object of the present invention to
19 provide a method for producing an improved electrocatalytic
20 cathode for use in an electrochemical cell.

21 It is a further object of the present invention to provide a
22 method for producing an improved electrocatalytic cathode as
23 above that is highly efficient toward catholyte reduction and
24 very stable.

25 It is still a further object of the present invention to
26 provide a method for producing an improved electrocatalytic
27 cathode as above which is capable of performing over a wide range

1 of energy densities and is suited for low powering endurance as
2 well as for high power applications.

3 The foregoing objects are attained by the method of the
4 present invention.

5 In accordance with the present invention, a method of
6 producing an electrocatalytic cathode for use in an
7 electrochemical cell system comprises the steps of providing a
8 carbon substrate and simultaneously depositing palladium and
9 iridium on the carbon substrate by cyclic voltammetry or by
10 controlled potential coulometry. The simultaneous deposition of
11 the palladium and iridium is preferably carried out using a
12 solution containing 1.0mM palladium chloride, 2.0mM sodium
13 hexachloroiridate, 0.2M potassium chloride, and 0.1M hydrochloric
14 acid.

15 Other details of the method of the present invention, as
16 well as other objects and advantages attendant thereto, are set
17 forth in the following detailed description and the accompany
18 figures.

19 20 BRIEF DESCRIPTION OF THE DRAWINGS

21 FIGS. 1a and 1b are polarization curves for various
22 catalysts on high density carbon and on carbon paper toward
23 reduction of hydrogen peroxide;

24 FIG. 2 is a photomicrograph of a palladium/iridium
25 combination on a high density carbon at 7000X magnification;

1 FIG. 3 is a graph showing semi-fuel cell voltages at various
2 current densities for catalyzed substrates after discharges at
3 100 mA/cm² for 3.75 hours;

4 FIG. 4 is a graph showing the long term stability on carbon
5 paper for four hours; and

6 FIG. 5 is a graph showing the variation of voltage with time
7 for both hydrogen peroxide and sodium hypochlorite at a constant
8 current density of 25 mA/cm².

9
10 DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

11 As previously discussed, the present invention relates to an
12 improved cathode for use in a semi-fuel cell and a method of
13 manufacturing or making same.

14 A cathode in accordance with the present invention is formed
15 by the simultaneous deposition of palladium and iridium on a
16 carbon substrate. The carbon substrate can be high density
17 carbon or carbon paper, which is a porous carbon.

18 The simultaneous deposition of the palladium and iridium on
19 the carbon substrate can be carried out by cyclic voltammetry or
20 by controlled potential coulometry. When used, the cyclic
21 voltammetry can be carried out at any one of a number of
22 potential ranges between -1.0V to +1.06V, preferably between
23 about -0.15V to +1.06V, vs. a silver/silver chloride (Ag/AgCl)
24 reference electrode and at any of a number of scan rates,
25 preferably from about 1.0 millivolt/sec to about 65
26 millivolts/sec. The degree of loading of the catalyst on the
27 carbon substrate can be controlled by the scan rate or by the

1 number of cycles, preferably from 5 to 45 cycles. Typically, the
2 simultaneous deposition of the palladium and iridium is carried
3 out by cyclic voltammetry at a potential from -0.150V to -0.300V
4 vs. silver/silver chloride at a scan rate of 10mV/s for 25
5 cycles. When using controlled potential coulometry, the
6 deposition is carried out at -0.25V vs. silver/silver chloride
7 for 10 minutes. Any of a number of potentials between 1.0V to
8 -1.0V vs. silver/silver chloride can be used. The degree of
9 loading, in this latter case, is controlled by the application of
10 the controlled potential for a time in the range of from about
11 3.0 to 10 minutes.

12 The solutions used for either of the above deposition
13 techniques are preferably heated to 70°C and preferably contain
14 1.0mM palladium (II) chloride, 2.0mM sodium hexachloroiridate
15 (IV) (Na_2IrCl_6), 0.2M KCl, and 0.1M HCl. A three electrode cell
16 consisting of the substrate, high density or carbon paper,
17 working electrode, a silver/silver chloride reference electrode,
18 and a platinum auxiliary electrode is preferably used for the
19 above depositions.

20 To show the improvements to be gained by the
21 platinum/iridium coated carbon cathode of the present invention,
22 a three electrode cell consisting of the catalyzed substrate as
23 the working electrode, a silver/silver chloride reference
24 electrode and a spectroscopic grade carbon rod counter electrode
25 was employed. Full cell performance was carried out using either
26 a 25 x 38mm cell made of polycarbonate and Teflon or a 38 x 200
27 mm cell made of Plexiglass. A Teflon insert used with the 25 x

38 mm cell permitted an electrode area of 1.0 cm^2 ($0.5 \text{ cm} \times 2.0 \text{ cm}$) to be used in the flow through cell as well as a 6.45 cm^2 ($2.5 \text{ cm} \times 2.5 \text{ cm}$) electrode. A Vexar spacer maintained the cell gap at 0.7 mm in both cells. The anode and cathode were mounted on individual current collector bus bars. The two electrodes were mounted vertically and were separated by the Vexar screen spacer. The catholyte and the electrolyte were pumped into the bottom of the cell, flowed between the anode and the cathode surfaces and exited at the top of the cell. A number of such cells were incorporated into a closed loop flowing electrolyte apparatus consisting, in series, of a heated electrolyte reservoir, a peristaltic pump, a heat exchanging coil in a constant temperature bath to maintain temperature, the flow through cell and a return to the reservoir. Cell current was regulated by means of a multistep load resistance substitution box and a dynaload. Cell current, voltage, inlet and outlet temperatures, and evolved gas flow rate were simultaneously monitored and recorded by a computer data logging system.

The aluminum anode was an ALUPOWERTM alloy designated EB50V. The electrolyte contained 3.0 M NaOH , $0.5 \text{ M H}_2\text{O}_2$ and 40 gram/Liter (g/L) of sea salt. Its temperature was maintained at 55°C and the flow rate was $100 \text{ cm}^3/\text{min}$.

Evolved gas was collected with a gas tight syringe from a T connection and rubber septum at the exit to the cell. Gas samples were taken several times during a particular use.

The gas samples were analyzed for $\text{H}_{2(\text{g})}$ and $\text{O}_{2(\text{g})}$ with a chromatograph such as a Hewlett Packard Capillary Gas

1 Chromatograph Model 5890 Series II Plus equipped with an HP PLOT
2 Molecular Sieve 5A column (30m x 0.32mm x 0.25 mm film thickness)
3 and a thermal conductivity detector.

4 Scanning electron microscopy was carried out using a JEOL
5 USA Model 6300 instrument. The SEM working distance was 15 mm
6 giving a resolution of 5.0nm.

7 A high density planar carbon substrate was found to support
8 the most uniform electrocatalytic surface. A comparison of the
9 catalytic performance of iridium alone, palladium alone, and a
10 palladium/iridium combination for the reduction of H_2O_2 in a
11 sodium hydroxide-seal salt electrolyte at 55°C on high density
12 carbon and on carbon paper is presented in FIGS. 1a and 1b. The
13 superior performance of the combination of Pd/Ir over the entire
14 current density range is clearly evident from these figures.

15 A scanning electron micrograph of the palladium-iridium
16 combination on the carbon substrate at 7000X magnification is
17 shown in FIG. 2. The clusters observed are reasonably spherical
18 and are uniformly distributed over the substrate surface. An
19 Energy Dispersive Spectrometry spectrum has confirmed the
20 presence of palladium and iridium on the surface. Oxygen is also
21 observed but no chlorine is found. Careful analysis of EDS
22 mapping shows the palladium, iridium, and oxygen to be at the
23 same locations on the surface.

24 A series of tests were carried out using a 30 x 200 mm
25 flowing test apparatus to quantify the efficiencies of the four
26 reactions which take place during cell discharge. The corrosion,
27 direct and decomposition reactions provide no useful electrical

1 energy. Only the electrochemical reaction produces electrical
2 energy. The following table illustrates the Al-H₂O₂ reactions.

4 TABLE I

5 Al-H₂O₂ Reactions

- | | | |
|---|-----------------------------|--|
| 6 | 1. Electrochemical Reaction | $2Al + 3HO_2^- \rightarrow 2AlO_2^- + OH + H_2O$ |
| 7 | 2. Corrosion Reaction | $2Al + 2H_2O + 2OH^- \rightarrow 2AlO_2^- + 3H_{2(g)}$ |
| 8 | 3. Direct Reaction | $2Al + 3H_2O_2 + 2OH^- \rightarrow 2AlO_2^- + 4H_2O$ |
| 9 | 4. Decomposition Reaction | $2H_2O_2 \rightarrow 2H_2O + O_{2(g)}$ |

10
11 The aluminum electrochemical efficiency is determined by
12 mass difference and integration of the current over time of the
13 experiment. The H₂O₂ electrochemical efficiency is determined by
14 the cerium (IV) titration of the H₂O₂, using 1,1-phenanthroline
15 iron complex as the visual indicator, at the start and at the end
16 of the experiment and integration of the current over time of the
17 experiment. The Al corrosion efficiency is based on the H_{2(g)}
18 analysis and the H₂O₂ decomposition efficiency is based on the
19 O_{2(g)} analysis. The percent direct reaction is obtained by
20 difference. These efficiencies are summarized in Table II. The
21 precision figures listed are based on triplicate determinations.

<u>Reaction</u>	<u>Percent Efficiency (Al based)</u>	<u>Percent Efficiency (H₂O₂ based)</u>
Electrochemical	54% ± 4.5	38% ± 2.5
Corrosion	25% ± 1.4	-----
Direct	23% ± 1.9	38% ± 0.8
Decomposition	-----	25% ± 2.2

Multiple Al-H₂O₂ semi-fuel discharges at 100 ma/cm² for 45 minutes followed by the acquisition of cell voltages at various current densities show continued catalytic activity and stable electrochemical performance for the Pd/Ir catalyzed carbon substrate. Semi-fuel cell voltages at various current densities for Pd/Ir catalyzed high density planar carbon and reticulated nickel, obtained initially (carbon and nickel plate) and after discharge at 100 mA/cm² for long duration (3.75 hours; carbon and nickel plate) are shown in FIG. 3. The cell performance using a silver foil baseline catalyst is included for comparison.

1 The voltage of the cell containing the Pd/Ir catalyzed
2 carbon, after 3.75 hours of H_2O_2 discharge, is higher than the
3 silver foil baseline by 70 mV in the 100 - 300 mA/cm^2 range and
4 is essentially identical to its initial performance. The voltage
5 of the cell containing Pd/Ir catalyzed reticulated nickel is
6 lower over the entire current range, both initially and after
7 3.75 hours of discharge, than the baseline silver foil. The
8 poorer performance of the cell incorporating catalyzed
9 reticulated nickel after discharge relative to its initial
10 performance is clearly evident.

11 Cell voltages measured at 250 mA/cm^2 for the Al- H_2O_2 semi-
12 fuel cell containing Pd/Ir catalyzed high density carbon after
13 successive discharges at 100 mA/cm^2 for forty five minutes were
14 as much as 380 mV higher than when a similarly catalyzed
15 reticulated nickel cathode was employed. Improved long term
16 performance was also demonstrated by the cell containing
17 catalyzed carbon. The cell voltage decreased to 1.00 V after
18 twelve forty five minute discharges at 100 mA/cm^2 whereas the
19 1.00 V level was obtained only after six forty-five minute 100
20 mA/cm^2 discharges with the cell containing catalyzed reticulated
21 nickel.

22 Long term stability of the Pd/Ir catalyst on carbon paper
23 (porous carbon) has been demonstrated. FIG. 4 shows the
24 exceptionally stable voltage that is achieved at 25 mA/cm^2 with
25 the aluminum-hydrogen peroxide semi-fuel cell incorporating a
26 Pd/Ir on carbon paper support cathode.

1 FIG. 5 depicts the performance of the palladium/iridium on
2 carbon catalyst in a magnesium-sodium hypochlorite semi-fuel
3 cell. This figure also shows the superior cell voltage obtained
4 with the palladium/iridium on carbon catalyst relative to a
5 palladium on reticulated nickel catalyst.

6 As can be seen from the foregoing, a palladium/iridium on
7 carbon cathode formed in accordance with the present invention
8 will yield higher cell voltages relative to a similar cell
9 incorporating a silver catalyst cathode or a palladium/iridium on
10 nickel substrate cathode and will demonstrate greater stability
11 relative to a similarly catalyzed nickel substrate cathode. A
12 palladium/iridium on carbon cathode formed in accordance with the
13 present invention will demonstrate improved long term
14 performances relative to a similarly catalyzed nickel substrate
15 cathode or a silver catalyst cathode and will yield increased
16 electrochemical efficiency relative to a similarly catalyzed
17 nickel substrate cathode or a silver catalyst cathode. Still
18 further, a palladium/iridium on carbon cathode in accordance with
19 the present invention can be used in a semi-fuel cell
20 incorporating an aluminum or magnesium anode, hydrogen peroxide
21 or hypochlorite catholyte and an acidic or basic catholyte
22 medium.

23 It is apparent that there has been provided in accordance
24 with the present invention an electrocatalytic cathode device of
25 palladium and iridium on a high density or porous carbon cathode
26 support and a method for making such a cathode which fully
27 satisfy the means, objects, and advantages set forth

1 hereinbefore. While the present invention has been described in
2 the context of specific embodiments thereof, other modifications,
3 variations, and alternatives will become apparent to those
4 skilled in the art having read the foregoing description.
5 Therefore, it is intended to embrace such modifications,
6 variations, and alternatives which fall within the broad scope of
7 the appended claims.